



(11) **EP 4 249 571 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
27.09.2023 Bulletin 2023/39

(51) International Patent Classification (IPC):
C10B 57/04 (2006.01)

(21) Application number: **21895219.0**

(86) International application number:
PCT/RU2021/050148

(22) Date of filing: **28.05.2021**

(87) International publication number:
WO 2022/108484 (27.05.2022 Gazette 2022/21)

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

- **TIMIN, Evgeny Nikolaevich**
Moscow, 108811 (RU)
- **DENISENKO, Elena Viktorovna**
Altai Kray, 659100 (RU)
- **VIUKOV, Dmitrii Sergeevich**
Lipetsk, 398046 (RU)
- **KAPUSTIN, Vladimir Mikhailovich**
Moscow, 119296 (RU)

(30) Priority: **19.11.2020 RU 2020138082**

(74) Representative: **Boskovic, Davor**
Producta d.o.o.
Zinke Kunc 3a
10000 Zagreb (HR)

(71) Applicant: **NLMK International B.V.**
1077 XX Amsterdam (NL)

(72) Inventors:
• **PRUS, Andrei Andreevich**
Moscow, 117638 (RU)

(54) **COMPOSITION OF A CHARGE FOR PRODUCING METALLURGICAL COKE**

(57) The invention relates to the coke industry, and more particularly to the composition of a charge for producing metallurgical coke. A charge of a special composition for the production of metallurgical coke is developed, the charge comprises:

- a blend of coals of caking groups: ranks G (gas coal) and/or GF (gas fat coal) and/or GFL (gas fat lean coal) and/or F (fat coal), and inert groups: ranks CC (coking low-caking coal) and/or LC (lean caking coal), in a ratio of 1:1.15; and
 - a petroleum coke produced by the delayed coking of heavy petroleum residues, which has a caking index of from 75 to 100 units,
- with the following ratio of components, wt. %:

blend of coals of caking and inert groups in a ratio of 1:1.15 - 60 to 93.5; and
petroleum coke - 6.5 to 40.

The technical effect is provision of a special charge composition comprising a blend of coals of caking and inert groups in a ratio of 1:1.15 in an amount of from 60 to 93.5 wt. %, and petroleum coke in an amount of from 6.5 to 40.0 wt. %, that makes it possible to produce metallurgical coke which exhibits improved strength characteristics (coke strength after reaction with CO₂ (CSR) in a range of from 60 to 66% and a coke reactivity index (CRI) in a range of from 23 to 28%).

EP 4 249 571 A1

Description

[0001] The invention relates to the coke industry and in particular to the composition of a charge for producing metallurgical coke.

[0002] It is known that in order to improve the technological characteristics of charges, to upgrade the quality of coke, and to save scarce coal ranks, it is proposed to use various organic additives, such as solid waste from coke production, petroleum coke breeze, non-caking coals, and other additives, while ensuring the strength characteristics of coke and reducing the cost of production.

[0003] There is a known charge used for metallurgical coke comprising a coking coal, a coke production waste plasticizer in the amount from 0.5 to 7 wt.% (RU No. 2333236, 10.09.2008), and bituminous residue from the process of producing light fractions of petroleum products, and having the following characteristics: ash content A^d is up to 2.5%; volatiles content V^{daf} is up to 70%; sulfur content S^d is up to 5%; swelling is not less than 20 mm; and Roga index (RI) is not less than 10 (RU No. 2418837, 20.05.2011).

[0004] A significant disadvantage of using the above inventions is the impossibility of using plastic components in the charge of coke production due to possible agglomeration of particles and sticking, the need to reconstruct technological equipment in a coal preparation or coke departments, as well as the possibility of replacing only certain ranks of coking coal due to a relatively low level of volatile substances.

[0005] There is a known method (RU No. 2663145, 01.08.2018) of producing a charge for coking, which comprises mixing a petroleum caking additive with low-caking coal ranks CC (coking low-caking) and/or CLCLM (coking low-caking low-metamorphosed coals), and/or CL (coking lean), and/or LL (lean low-caking) and/or LC (lean caking) in the following ratio of components, wt.%:

- petroleum caking additive - from 1 to 30,
- low-caking coals - from 99 to 70.

[0006] The petroleum caking additive is a petroleum refining residue having the following characteristics:

- ash content A^d - up to 2.5%;
- volatiles content V^{daf} - up to 90%;
- sulfur content S^d - up to 5%;
- ring-and-ball softening point - not less than 40°C.

[0007] The disadvantage of this invention is the lack of technologies for supplying components in a liquid-flow state to the coal charge and, as a result, the impossibility of applying the invention in an industrial scale.

[0008] There is a known charge composition used for coking and comprising a petroleum additive being the product of delayed semi-coking of heavy petroleum residues with a volatile content of 12 to 28 wt.%. (RU No. 2355729, 20.05.2009; No. 2411283, 10.02.2011; RU No. 2563493, 2015; RU No. 2637965, 08.12.2017).

[0009] The disadvantage of the additive according to these patents is the instability of its caking properties, the insufficient coking level of the additive and, accordingly, the unstable quality of the resulting metallurgical coke, as well as the lack of a description of clear boundaries for the use of this product in the composition of the charge for coke production, which causes difficulties in assessing the effect of the presence of this product on the quality of metallurgical coke.

[0010] Further, there is a known blend of petroleum coke used in the charge composition in the amount of 1-30 wt.% and petroleum residues in the amount of 1-30 wt.%.

[0011] The used petroleum residues are characterized by ash content A^d of up to 2.5%, volatiles content V^{daf} of up to 90%, sulfur content S^d of up to 5%, and Roga index (RI) of less than 10. The petroleum coke is characterized by ash content A^d of up to 2.5%, volatiles content V^{daf} of up to 25%, and sulfur content S^d up to 5% (RU No. 2627425, 08.08.2017).

[0012] A significant disadvantage of using the invention is the need to reconstruct the process equipment in the coal preparation or coke departments.

[0013] The closest composition of the charge for coking is the composition of the charge proposed in the method for producing metallurgical coke (RU No. 2553116, 2015), which is used as a carbonaceous charge with a content of from 50 to 100 wt.% of petroleum semi-coke with a volatiles content of from 14 to 25 wt.% produced by delayed partial carbonization of heavy petroleum residues.

[0014] The disadvantage of the described method using a carbonaceous charge is the difficult use of the equipment made specifically for this method.

[0015] The problem to be solved by the invention is to develop a special coking charge composition, which makes it possible to expand the range and reduce the cost of the raw materials of the used charge with an improvement in the quality of metallurgical coke having higher strength characteristics (coke strength after reaction with CO_2 (CSR) in the range of from 60 to 66% and coke reactivity index (CRI) in the range of from 23 to 28%).

[0016] This problem is solved by developing a special coking charge composition for producing metallurgical coke, comprising:

- a blend of coals of caking groups: ranks G (gas coal) and/or GF (gas fat coal) and/or GFL (gas fat lean coal) and/or F (fat coal), and inert groups of ranks CC (coking low-caking coal) and/or LC (lean caking coal) in a ratio of 1:1.15 (a blend of coals of caking groups comprises coals of ranks G, GF, GFL, F, as well as coals of LC and CC ranks within the blends of inert groups, respectively, can be used as interchangeable without deterioration of characteristics of the resulting coke),
 - a petroleum coke produced by the delayed coking of heavy petroleum residues, which has a caking index of from 75 to 100 units,
- with the following ratio of components, wt.%:

blend of coals of caking and inert groups in a ratio of 1:1.15 - 60 to 93.5; and
petroleum coke - 6.5 to 40.

[0017] The charge composition uses petroleum coke produced by delayed coking of heavy petroleum residues: tar, deasphalting asphalt, vacuum visbreaking residue, etc.

[0018] The experiments conducted by the authors of the present invention with charges of various rank composition at a ratio of coals of caking and inert groups of 1:1.15 with petroleum coke added to the blend in an amount of from 6.5 to 40 wt.% showed that it is possible to produce metallurgical coke having improved strength characteristics.

[0019] The possibility of replacing the coal component with petroleum coke is explained by the fact that petroleum coke has a dual effect on the caking process: it acts on the one hand as a lean additive, and on the other hand, as a caking component, since petroleum coke comprises liquid products and can affect the pyrolysis processes of carbon mass.

Exemplary embodiments

Example 1

[0020] For the implementation of the invention, the used charge for the coke production had the following composition, wt.%:

$(G + GF + GFL + F) = 43.5 \text{ wt.}\%$; $CC = 50.0 \text{ wt.}\%$; petroleum coke = 6.5 wt. %

$(G + GF + GFL + F) : (CC) = 1-1.15$;

Table 1 represents the qualitative characteristics of petroleum coke.

Table 1

	Parameter	Unit	Value
1	Ash content A^d	%	0.4
2	Volatiles content V^d	%	15-18
3	Total sulfur content S^d	%	4.0-4.8
4	Coke strength after reaction CSR	%	55-70
6	Coke reactivity index CRI	%	23-28
7	Caking index G, GOST ISO 15585-2013	-	75-100

[0021] Similarly, for the implementation of the invention, the used charge according to examples 2 and 3 had a ratio of caking and inert coal groups of 1:1.15. Table 2 represents the qualitative characteristics of metallurgical coke depending on the charge composition and the amount of petroleum coke used.

Table 2

Charge version	Charge composition, %			Physical and chemical properties of metallurgical coke, %				
	G + GF + GFL + F	CC/LC	Petroleum coke	W ^r	A ^d	S ^d	CSR	CRI
Basic	46.5	53.5	0	0.2	11.1	0.52	57.2	30.0
Experimental 1	43.5	50.0	6.5	0.2	10.4	0.75	60.4	28.0
Experimental 2	38.6	44.4	17.0	0.2	9.3	1.15	63.8	24.3
Experimental 3	27.9	32.1	40.0	0.2	6.9	1.85	65.8	23.1
where W ^r is total moisture content (%); A ^d is ash content (%); S ^d is total sulfur content (%); CSR is coke strength after reaction with CO ₂ (%); and CRI is coke reactivity index (%).								

[0022] As follows from the data given in Table 2, charges comprising blends of caking and inert coal groups of various ranks in the ratio of 1:1.15 in the amount of from 60 to 93.5 wt.% and petroleum coke in the amount of from 6.5 to 40 wt.% can be used to produce metallurgical coke with improved strength characteristics: coke strength after reaction with CO₂ (CSR) in the range of from 60 to 66% (57% in the basic version) and coke reactivity (CRI) in the range of from 23 to 28% (30% in the basic version).

Claims

1. A charge of a special composition for the production of metallurgical coke, comprising

- a blend of coals of caking groups: ranks gas coal and/or gas fat coal and/or gas fat lean coal and/or fat coal, and inert groups: ranks coking low-caking coal and/or lean caking coal, in a mass ratio of 1:1.15; and
 - a petroleum coke produced by the delayed coking of heavy petroleum residues, which has a caking index of from 75 to 100 units (GOST ISO 15585-2013),
- with the following ratio of components, wt.%:

blend of coals of caking and inert groups in a mass ratio of 1:1.15 - 60 to 93.5; and
petroleum coke - 6.5 to 40.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2021/050148

A. CLASSIFICATION OF SUBJECT MATTER

C10B 57/04 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10B 57/04, 57/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSearch (RUPTO Internal), USPTO, PAJ, Espacenet, Information Retrieval System of FIPS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	RU 2637699 C1 (OTKRYTOE AKTSIONERNOE OBSHCHESTVO "ALTAI-KOKS") 06.12.2017, page 4, line 36- page 5, lines 7, 10-13	1
Y	EA 021524 B1 (OTKRYTOE AKTSIONERNOE OBSHCHESTVO "GUBAKHINSKII KOKS") 30.07.2015, page 1, paragraph 7 on the top	1
Y	SU 1736993 A1 (VSESOIUZNYI NAUCHNO-ISSLEDOVATELSKII INSTITUT OKHRANY TRUDA I TEKHNIKI BEZOPASNOSTI CHERNOI METALLURGII) 30.05.1992, column 3, lines 25-40	1
Y	RU 2627425 C1 (OBSHCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU "PROMINTEKH NKA") 08.08.2017, page 3, lines 34-38, page 4, lines 7-9, page 5, lines 44,45, page 6, lines 3-6	1
Y	VESELOVSKII V. S. Ugolnye i grafitovye konstruktsionnye materialy. Izdatelstvo "Nauka". Moscow, 1966, 226, page 121, Deistvie otoshchaiushchikh dobavok	1

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

06 October 2021 (06.10.2021)

Date of mailing of the international search report

07 October 2021 (07.10.2021)

Name and mailing address of the ISA/

Authorized officer

Facsimile No.

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- RU 2333236 [0003]
- RU 2418837 [0003]
- RU 2663145 [0005]
- RU 2355729 [0008]
- RU 2411283 [0008]
- RU 2563493 [0008]
- RU 2637965 [0008]
- RU 2627425 [0011]
- RU 2553116 [0013]